Office of the Principal, S.P.C. Govt. College, Ajmer

No- 1983

Date - 9/5/16

CERTIFICATE

This is to certified that Ms. Bharti Chaturvedi Daughter of Mr. Vidhyanand chaturvedi has qualified the Course Work of Paper-II and III for Registration for the Ph.D. programme in the Department of Chemistry of the S.P.C. Govt. college, Ajmer on...6/5/16

Signature with date 6/6/16

Supervisor

Lecturer.....
Samrat Prithviraj Chauhan
Govt. College, Ajmer

Signature with date

Head of the Institution

Principal
Samrat Prithviraj Chauhan
Govt. College, Ajmer

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Receipt No. 1808 / 9.5.16 (MDS)

(6)

Office of the Principal, Government College, Ajmer

No. 1983 **Date** 9/5/16

To,

The Director (Research)

Maharshi Dayanand Saraswati University,

Ajmer- 305001 (Rajasthan)

Sub - Synopsis for registration of Ph.D. degree in chemistry

Sir,

Enclosed please find herewith four copies of synopsis entitled **"MICROWAVE ASSISTED SYNTHESIS AND CHARACTERIZATION OF O-ALKYL AND O-ARYL TRITHIOPHOSPHATES OF SOME TRANSITION METAL ELEMENTS"** of **Bharti Chaturvedi** for the registration of Ph.D. degree (Chemistry) under supervision of **Dr. Alok Chaturvedi** in the subject of Chemistry.

Kindly acknowledge the same.

Yours Sincerely,

(Principal)
S.P.C. Govt. College, Ajmer

Principal
Samrat Prithviraj Chauhan
Govt. College, Ajmer

Enclosed - Four copies of synopsis.

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To,

The Director (Research)

Maharshi Dayanand Saraswati University,

Ajmer – 305001 (Rajasthan)

Through – Principal, S.P.C. Government College, Ajmer

Sub – Submission of synopsis in chemistry.

Sir,

I am submitting four copies of synopsis entitled **"MICROWAVE ASSISTED SYNTHESIS AND CHARACTERIZATION OF O-ALKYL OR O-ARYL TRITHIOPHOSPHATES OF SOME TRANSITION ELEMENTS"** for registration of Ph.D. in chemistry under supervision of **Dr. Alok Chaturvedi,** Lecturer, S.P.C. Government College, Ajmer.

Yours sincerely,

Bharti Chaturvedi

(Bharti Chaturvedi)

Research Scholar

Dr. Alok Chaturvedi

Lecturer (selection scale)

Department of Chemistry

S.P.C. Govt. College, Ajmer

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MICROWAVE ASSISTED SYNTHESIS AND CHARACTERIZATION OF O-ALKYL OR O-ARYL TRITHIOPHOSPHATES OF SOME TRANSITION ELEMENTS

"कुछ संक्रमण तत्वों के O-ऐल्किल/O-ऐरिल ट्राइथायोफॉस्फेटों का सूक्ष्मतरंगों की सहायता से संश्लेषण एवं उनके अभिलक्षण"

A

SYNOPSIS

Submitted for the Award of Ph.D. degree of

Maharshi Dayanand Saraswati University, Ajmer

In the Faculty of Science (Chemistry)

By

Ms. Bharti Chaturvedi

Under Supervision of

Dr. Alok Chaturvedi

Lecturer (Selection scale)

Department Of Chemistry

S.P.C. Govt. College, Ajmer.

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APPENDIX – IV

Format for outline of Proposed Research Work

(To be supplied in Eight copies)

1. Name of scholar
   (In English) : - **Ms. BHARTI CHATURVEDI**
   (In Hindi) : - भारती चतुर्वेदी

2. Title of Research Work
   (In English) : - **MICROWAVE ASSISTED SYNTHESIS AND CHARACTERIZATION OF O-ALKYL OR O-ARYL TRITHOPHOSPHATES OF SOME TRANSITION ELEMENTS**

   (In Hindi) :- "कुछ संक्रमण तत्वों के 0-ऐल्किल/0-ऐरिल ट्राइथायोफॉस्फेटों का सूक्ष्मतरंगों की सहायता से संश्लेषण एवं उनके अभिलक्षण"

3. Location : - **DEPARTMENT OF CHEMISTRY, S.P.C. GOVT. COLLEGE AJMER**

4. Importance of proposed investigation, objectives : - **Annexure - 1**
5. Review of work already done on the subject of proposed research study : - **Annexure - 2**
6. Research gaps identified in the proposed field of investigation : - **Annexure - 3**
7. Major hypothesis, if any : - **Annexure - 4**
8. Research methodology : - **Annexure - 5**
9. Bibliography : - **Annexure - 6**

Name & Signature of Supervisor
with date & seal Dr. Alka Chaturvedi 6/5/16

Banwari Prasad Yadav Chauhan
Govt. College, Ajmer

Bharti Chaturvedi
Signature of Candidate
with date 6/5/16

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Annexure – I

Importance of Proposed Investigation

In microwave chemistry, microwave irradiations apply to chemical reactions[1-3]. It requires milder reaction condition and lower energy, gives higher chemical yield of products. It accelerates the reaction rate of the reaction.

The organic derivatives of transition metals with sulphur and phosphorus containing ligands have important place in metallo-organic chemistry[4-8], because these compounds have wide biological[9], antifungal[10], antimicrobial[11], antitoxic and industrial applications[12].

The compounds have interesting structural features due to unusual bonding modes between metal and sulphur – phosphorus containing ligands of complexes.

In last few decades chemists are taking interest in the chemistry of metallic and organometallic complexes of phosphoric and thiophosphoric acids. These organometallic compounds are widely used as pesticides[13], insecticides[14], bacteriocides[15], etc. Due to this every year thousands of patents are registered on these complexes.

Aliphatic thiophosphates (R_1O) (R_2O) $(R_3S)PO$, aliphatic dithiophosphates (R_1O) (R_2S) $(R_3S)PO$ and aliphatic trithiophosphates (R_1S) (R_2S) $(R_3S)PO$ in which R_1, R_2, R_3 can be the same or different, are used in defoliation, improvement in crop value and indirect control of pest invfestation[16].

By mixing of organoaluminium compound, a titanium trihalide and trithiophosphate a solid highly crystalline poly-olefins obtained which comprises the polymerizing of alpha- olefins with a three component catalyst system[17]. Esters of o-alkyl trithiophosphate used as defoliants[18], insecticides[19], nematodicides and inhibitor of steel corrosion[20].

On the basis of above importance of trithiophosphate complexes we have planned to synthesized metal (Fe, Ru, Ni) derivatives of O-alkyl or O-aryl trithiophosphates.

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Objectives

Objectives of the proposed study are as given below :-

1. To explore greener approach for synthesis of O-alkyl or O-aryl trithiophosphates.
2. To minimize energy consumption, higher yield of product, minimize use of solvent and eco-friendly synthesis.
3. To synthesize O-alkyl or O-aryl trithiophosphate derivatives of transition metal like – Fe, Ru, Ni.
4. Characterization of the newly synthesized derivatives by elemental analysis (C,H,S,metal), molecular weight measurements and electrical conductivities.
5. To characterize and analyse derivatives with the help of the spectroscopic studies i.e. IR, NMR (^{1}H, ^{13}C, ^{31}P etc).
6. By the use of paper disc method screening of newly synthesized derivative as antibacterial agent.
7. To compare their antibacterial activity with standard drugs.

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Annexure – II

Review of Work Already Done on the Subject of Proposed Research Study

A large number of metal derivatives of thiophosphates and dithiophosphates have been synthesized. These derivatives show different chemical bonding viz: monodentate, bidentate, bridging and chealating.However a little information is available on the O-alkyl or O-aryl trithiophosphstes complexes[21].

Diorganotin(IV) S-alkyltrithiophosphates are prepared[22] by the reaction of diorganotin dichloride and S-alkyl trithiophosphates in equal ratio in anhydrous benzene.

$$R_2SnCl_2 + (R'S)P(O)(SK)_2 \longrightarrow R_2Sn[S_2(O)P(SR')]$$

(R = Me, Et, Bu, Ph; R' = Me, Pri, Ph)

The antifungal complexes of acetylacetonatodiorganotin(IV)-O-alkyl trithiophosphates synthesized[23] by the reactions of dialkyltin dichloride with acetylacetone and O-alkyl trithiophosphates in a 1:1:1 molar ratio in dry benzene. The obtained complexes are monomeric and light yellow coloured crystalline solids. Spectral studies showed that in the complexes acetylacetonate and O-alkyl trithiophosphate moieties are bidentate and tin is in hexacoordinated in nature.

Dichlorotitanium(IV) trithiophosphate $TiCl_2[(RO)P(S)S_2]$ (where R = Me, Et, Pr^n, Pr^i, Bu^n, Bu^i, Am^i, Ph and cyclohexyl) have been synthesized[24] by the reaction of titanium tetrachloride and potassium trithiophosphate in 1:1 molar ratio in anhydrous benzene.

Boron derivatives of O-alkyl trithiophosphate $ROP(S)S_2[BS_2P(S)OR]_2.2NMe_3$ (R = Me, Et, Pr^i, Bu^i, Ph,CH_2Ph) were synthesized[25] by the reactions of trimethylaminoborane with O-alkyl or O-aryl trithiophosphates in 2:3 molar ratio in dried and distilled benzene. The derivatives consistent with four coordinated boron and bidentatebehaviour of the trithiophosphate moiety.

To synthesized[26]arsenic(III) O-alkyl or O-aryl trithiophosphate by solvent free microwave assisted procedure, reaction is carried out in between the arsenic trichloride with dipotassium salt of O-alkyl or O-aryl trithiophosphate in 1:1 and 2:3 molar ratio.

Aluminium(III) derivatives of O-alkyl or aryl trithiophosphate of the formula $Al[S_2P(SH)OR]_3$ (R=Me, Et, Pr^i,Bu^i, Ph,CH_2Ph) have been synthesized[27]. The products were obtained as white powdery solids and also have antifungal effectiveness against powdery mildew disease.

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Reaction of dipotassium salts of O-alkyl trithiophosphate with acetyl, benzyl and benzoyl chloride yield[28] substituted organic esters $ROPS_3(C_6H_4CH_2)_2$ and $ROPS_3(RCO)_2$. The compounds are white crystalline solids and soluble in DMSO. The complexes have distorted tetrahedral geometry.

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Annexure - III

Research Gaps Identified in the Proposed Field of Investigation

The metal and organometal derivatives of O-alkyl dithiophosphates are widely used due to their interesting bonding modes and applications in various fields. Literature of survey reveals that much work has been carried out on metal derivatives of O-alkyl and O-aryl mono and dithiophosphates[29-34]. O-alkyl trithiophosphate ligand is ambidentate and can form different types of metal-oxygen/phosphorus bonds hence various organometallic complexes are formed.

Different types of sulphur containing ligands like thiolates, dithiolates, thio-β-di-ketonates, dialkyl and alkylene dithiophosphates with metals or organometals have been studied earlier in our as well as different other laboratories.

Organic esters of trithiophosphoric acids are well known but the organometallic esters are unknown as yet. The synthesis of organometallic ester derivatives opens a new area of research.

Although a few metal (B,Sn,As,Sb) derivatives of O-alkyl and O-aryl trithiophosphates are synthesized[35-37] yet survey of literature reveals that no research work has been done on the synthesis of O-alkyl trithiophosphates derivatives of metal (Fe, Ru, Ni) and also their antifungal and antibacterial activity.

Due to this it was considered to synthesize O-alkyl or O-aryl trithiophosphate complexes of transition metals like Fe, Ru, and Ni and characterize them with various physio-chemical as well as spectroscopic techniques.

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Annexure - IV

Major Hypothesis, If Any

Metal derivatives and organic esters of trithiophosphates have a wide range applications. The complexes may be synthesize by the following steps which are mentioned below :-

- **Preparation of Ligand–**

1. Dipotassium salt of O-alkyl trithiophosphte may be synthesized by the following two steps-

(A) A suspension of P_2S_5 in benzene is made in R.B.F. A mixture of triethylamine and appropriate amount of alcohol may added drop-wise to the suspension in a manner that the solvent being to boil uniformly. Two layers are formed.

(B) In the next step after separating the upper layer, methanolic solution of 1 mol KOH will added to the lower layer. Dipotassium salt of O-alkyl trithiophosphate will formed.

$$P_2S_5 + Et_3N + ROH \longrightarrow K_2S_3POR$$

(R= Me, Et, Pr^i, Bu^i, Ph)

Ligand may prepare by traditional method as mentioned above or alternatively by microwave method.

- **Reaction of metal compound with ligand–**

After the formation of dipotassium salt of O-alkyl trithiophosphate, its reaction will be carried out with metallic halides of some transition metals viz. – Fe, Ru, Ni to form their metal derivatives of O-alkyl trithiophosphates. For this purpose microwave assisted synthesis will be use.

$$MX_3 + K_2S_3POR \xrightarrow[\text{Solvent free atm.}]{\text{Microwave irradiation}} XM(S_3POR)_2 + 2KX$$

$$MX_2 + K_2S_3POR \xrightarrow[\text{Solvent free atm.}]{\text{Microwave irradiation}} M(S_3POR)_2 + 2KX$$

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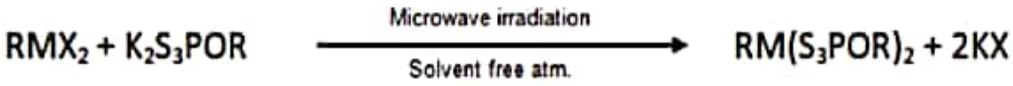

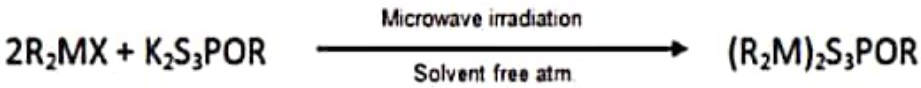

(M = Fe, Ru, Ni)

(R = Me, Et, Pr^{i}, Bu^{t}, Ph, $C_6H_5CH_2$-)

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Annexure – V

Research Methodology

1. Eco-friendly, microwave assisted synthesis for O-alkyl or O-aryl trithiophosphates will be use during the research tenure.

2. Synthesis of O-alkyl trithiophosphate by the reaction of phosphorus pentasuphide, appropriate alcohol and triethylamine followed by the adding of 1 mol KOH in methanol medium.

3. Methanol, ethanol, isopropanol and isobutanol, phenol, benzyl alcohol, cresol will be used to synthesize of dipotassium salt of O-alkyl trithiophosphate.

4. Metal halide and organometallic halide and dipotassium salt of O-alkyl trithiophosphate react together and formed metal derivatives of O-alkyl trithiophosphate.

5. Compounds of $RM(S_3POR)_2$ (where M = Fe, Ru, Ni and R = Me, Et, Pr^i, Bu^i, Ph) will be formed by the reaction of RMX_2 and K_2S_3POR by solvent free microwave irradiation method.

6. By elemental analysis, molecular weight measurements, IR and NMR (^1H, ^{13}C, ^{31}P) spectral studies structure of newly synthesized O-alkyl trithiophosphate metal derivative will be characterize. On the basis of different absorption bands obtain in spectral studies and by the physico-chemical parameters the structure and coordination behaviour of central metal atom will be predicted.

7. By using different standard method like – paper disc method and radial growth method for antibacterial and antifungal activity, study will be carried out. Biological activity of newly formed derivatives will compare with standard drugs.

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Chapter-wise Detail of Proposed Work

TITLE - MICROWAVE ASSISTED SYNTHESIS ANDCHARACTERIZATION OFO-ALKYL OR O-ARYLTRITHIOPHOSPHATES OF SOME TRANSITION ELEMENTS

The entire research work will be divided into following chapters : -

Chapter - 1 Introduction

Chapter - 2 Review of Literature

Chapter - 3 Experimental (Methods and Materials)

Chapter - 4 Results and Discussion

Chapter - 5 Summary

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